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Summary Report on Task 3- Immobilisation Process/Equipment Testing

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by

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The following work covers progress in Task 3 up to the revised reporting date of 15th April 1999 - as per the scope of work B345772, dated Sept 9, 1998.

3.1 Attrition Milling/Blending Studies

3.1.1 Attrition Mill Discharge Agents

Ethylene Bi-Stearamide (EBS) aids in the discharge of powders from the attrition mill. Local suppliers have provided us with two types of EBS, KAOWAX and UNIWAX, from Kao Corporation and Lion Chemical Company respectively.

Photomicrographs of the two EBS samples are shown in Figure 1 and the burnout characteristics in Figure 2 & 3.

3.1.2 MnO Attrition Grinding Trials

An attrition grinding trial using MnO powder (96% <150µm, 99%<250µm, AUSMINCO Pty Ltd) using a zirconia lined, 1.5 gallon 1SD Union Process mill, with Ø5mm zirconia balls has been completed. Particle size reduction demonstrated by the change in particle size distribution is shown in Figures 4, 5 & 6. These runs did not involve use of the KAOWAX discharge agent.

Problems with commissioning the high speed, steel lined, 1.3 gallon, HAS -1 pot have delayed MnO milling trials at 1000 and 1500rpm.

3.1.3 Blending of Precursor Components

Nine precursor blending runs have been completed. The process conditions for these are shown below.

Mill Body:	1SD attrition mill
Milling Media:	13.2 kg of Ø5 mm ZrO_2 beads
Powder Batch size:	1000g
Milling Medium:	2.2 litres of distilled water
Mill Speed:	250rpm
Milling Duration:	15 mins
Slurry Removal Aid:	further 200ml of distilled water
Slurry Drying:	pan dried at 110°C overnight
Calcination:	in alumina trays at 750°C in air for 2 hrs

Table 1 shows results from blending run TEX991011. The total batch size was 1010g, which included 10g of KAOWAX.

3.1.4 Precursor – U/Pu Surrogate Blending

The nine batches of blended precursor powders were mixed with CeO_2 powder (PuO_2/UO_2 surrogate) to form the Ce-baseline composition (A-0). Standard preparation for a 1kg batch is shown below.

Mill Body:	1SD attrition mill
Milling Media:	13.2 kg of Ø5 mm ZrO_2 beads
Powder Batch size:	1000g (passed through in 100g lots)
Milling Medium:	Dry
Mill Speed:	450rpm
Milling Duration:	5 mins / 100g lot

725.9g of blended precursor powder and 274.1g of CeO_2 powder were weighed into a container and tumble mixed for 5 mins, (NB if a discharge aid was to be introduced, it was also added at this point). The batch was then split into 10 x 100g lots to feed through the mill.

The Union Process 1SD zirconia lined attrition pot was also used for the precursor – CeO_2 blending process. The mill was brought up to an operating speed of 450 rpm prior to adding the

powder. Under these conditions the measured torque and power levels were 12 Nm and 76 HP respectively.

3.1.5 Media Wear

14.8g of zirconia was lost from the 13.2 kg charge of Ø5mm zirconia balls used in the 1SD zirconia lined attrition pot, after 11 x 1 kg-powder batches had passed through the mill. This was equivalent to incorporating an additional 0.13 wt% of ZrO_2 into the powder batches.

3.2 Granulation

3.2.1 Pan Granulator

Three granulation runs using attrition blended powder have been. Details of these runs are shown in Table 2.

Alterations have been made to the granulation apparatus such that 500 g and 1000 g batches of powder can be processed. During commissioning and process optimisation alumina powder was used in all granulation experiments.

Introduction of binders into the powder precursor was achieved by one of the following;

- Intimate mixing of powdered binder with the blended precursor / ceria powders, prior to the granulation treatment. Granules were formed by spraying water onto the powder bed.
- For binders in aqueous solution, by spraying directly onto the powder bed.

The binders investigated include:

1) Polyethylene glycol (PEG)	Powder form PEG 8000 (Aldrich Chemicals)
2) Polyvinyl alcohol (PVA)	In solution : 50% PVA (Daystar Chemicals)
	Powder form: Elvanol (Dupont)

3.3 Binder Burnout and Sintering Schedule

3.3.1 Puck Pressing Die

A number of alterations have been made to the uniaxial pressing die. These include; a) machining an overall 1° taper to aid in ejection of the pressed puck, b) purchase of a suitable spring to allow pseudo-double action pressing, c) installation of a pneumatic lifting device to aid in handling the die.

Powders from granulator runs G113 and G114 were pressed at 3000 psi (NB. delamination occurred during pressing at the baseline standard 2000 psi).

3.3.2 Sintering Runs

Two pucks pressed from granulated powders (G113 and G114) processed have been sintered using the baseline heat treatment, ie. 3 °C/min to 300 °C, hold 2 hr, 5 °C/min to 1350 °, hold for 4 hrs, cool to room temperature at 5 °C/min. Table 3 shows the shrinkage and density achieved in these runs. Figures 7 & 8 show photographs of the sintered pucks; Figure 8 shows the setup we have now adopted for sintering the pucks, previously all pucks were sintered on Pt sheets, but we now use zirconia grit on alumina discs. With the Ce/Ce baseline composition (A-0), only a few zirconia particles were found to adhere to the puck.

3.4 Non-destructive Evaluation

X-Ray Diffraction (XRD) analysis using a Scintag X1 Advanced Diffractometer System employing Cu K-alpha radiation has been performed on Th/U doped samples. These were prepared by the oxide-route, wet milled for 16 hrs and sintered at 1350°C for 4 hrs in air and argon. XRD analysis, was performed on samples made from the following compositions:

- B1-2 Baseline ceramic
- B1-4 Baseline ceramic + impurities
- B1-10 Zirconolite-rich
- B1-12 Brannerite-rich
- B1-14 "Nominally" 10 % perovskite doped (NB. this formulation does not produce perovskite under the above processing conditions)
- B1-16 ~ 10 % Phosphate-doped.

The top and bottom surfaces of the sintered pellets were examined by X-ray diffraction (XRD). Selected surfaces were examined by scanning electron microscopy (SEM).

The Ar sintered pellets were crushed to a fine powder, mixed with gum tragacanth (a binder) and tungsten metal (as an internal standard), and pressed into XRD sample holders for analysis. This work is almost complete; some of the samples need to be repeated to obtain a less noisy pattern.

The air sintered pellets had their top surfaces polished to remove the surface layer and are currently being examined by XRD. These pellets will be crushed and analysed as per the Ar samples.

Preliminary results of the Ar sintered samples indicate that the top and bottom surfaces and the powder samples have similar XRD patterns, with the few exceptions given below. The top surfaces were observed by SEM and were found to be similar, in terms of phases present, to the polished internal sections of previously examined samples from the same powder batches.

The following exceptions were noted in the Ar sintered samples:

- There is possibly some orientation of the brannerite in the bottom surface of the B1-2, B1-4 and B1-16 pellets, e.g. the 3.02 Å peak is more intense than in the top surface.
- The B1-12 (brannerite-rich) pellet may have slightly more brannerite on the bottom surface.

Figures 9 and 10 show images of the centre and surface of samples mws980137 and mws980434 respectively. These were both Task 1.2 samples of composition B1-2 made from oxide-route powders that had been wet-milled for 16 hours. Both samplers were sintered at 1350°C in Ar for 4 hours.

For the interior of sample mws980137, a Ø10 mm pellet, the matrix is pyrochlore. Th / U-brannerite, Hf-doped rutile, a trace of 4M zirconolite (4M), a grain of ThO_2 (O, white) and porosity (A) were also present.

Phases detected on the surface of mws980434, a Ø25 mm pellet, were pyrochlore, Th / U-brannerite and Hf-doped rutile. Porosity was also present.

There was approximately 15 – 20 vol. % brannerite on the surface of sample mws980434, compared to approximately 30 vol. % in the interior of sample mws980137. The amount of rutile in both samples was approximately the same at 2 – 3 vol. %.

Analysis of the corresponding air sintered samples is still to be completed. Preliminary XRD results indicate that the top and bottom surfaces of these samples are similar, except that there may be slightly more brannerite on the bottom surface.

3.5 Recycle of Unacceptable Materials

A sintered puck (SLDRUN990414), which had undergone the baseline sintering schedule, was crushed and milled to produce powder for recycling experiments.

This puck was introduced directly into a jaw crusher with a jaw gap of 3 mm. The 264 g sample was crushed in less than 30 seconds. The resultant shards were then fed slowly into a laboratory scale hammer mill with a grate over the exit port. The grate consisted of a matrix of Ø0.6 mm diameter holes. The total feed time to pass all the material through the mill was approximately 5 mins. A suction hose was used to remove any fines escaping from the mill. 256 g of powder was obtained after crushing and milling. The resultant powder was sieved using 1000 µm and 500 µm

sieves. 95 % of the powder passed through the 500 µm sieve with 6 % being > 500 µm and < 1000 µm.

This powder will be attrition milled prior to being introduced back into the blending stage of the process.

3.6 Provide Design Guidance / Review

Dr. A. Jostsons and Mr. R. Gray of ANSTO participated in the Plutonium Immobilisation Project, FY 99 Mid-Year Project Review for at the Lawrence Livermore National Laboratory, February 24 – 25, 1999

KAOWAX UNIWAX

>1000µm

>500µm

>250µm

<250µm

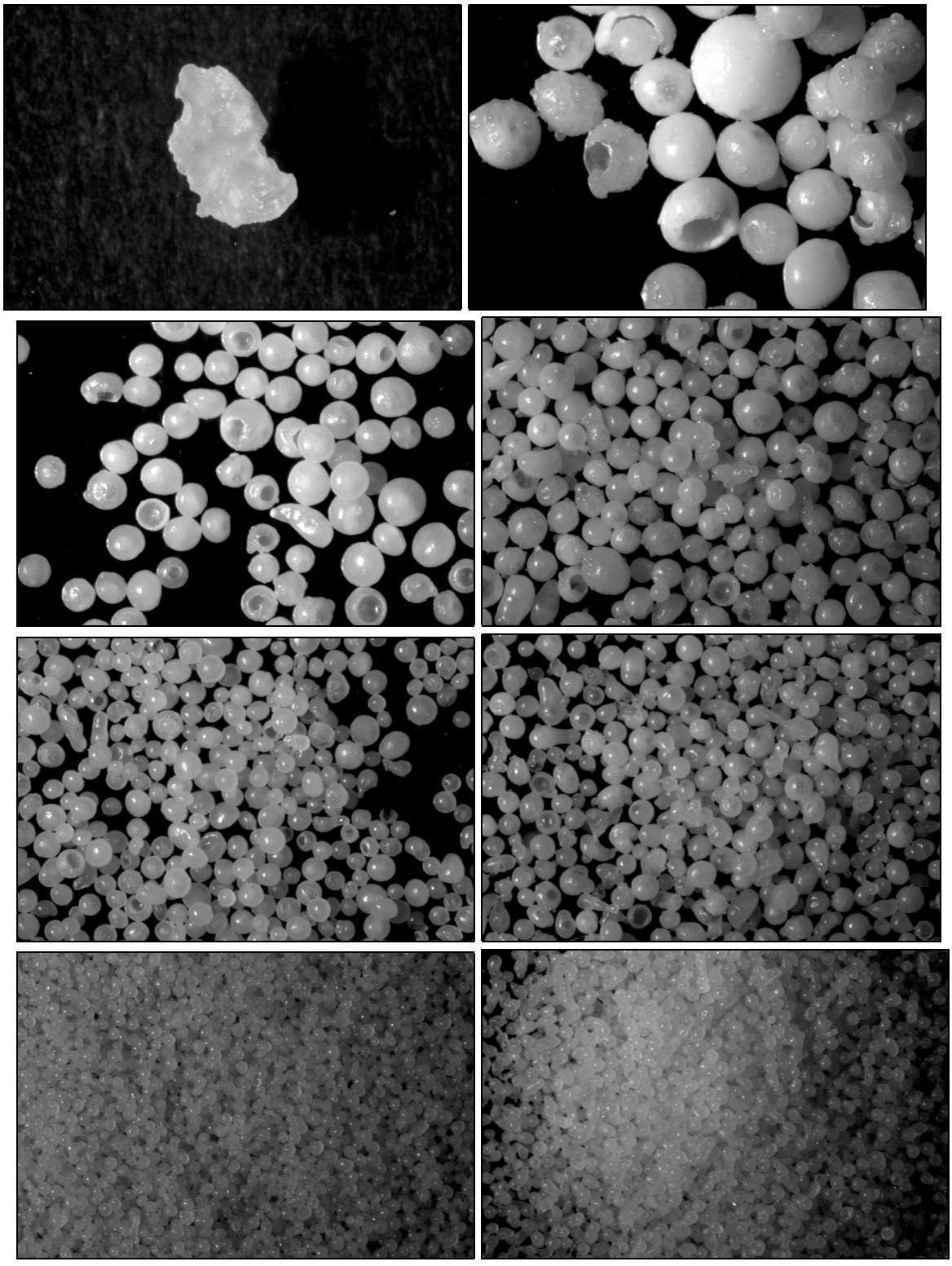


Figure 1 Photomicrographs comparing KAOWAX and UNIWAX

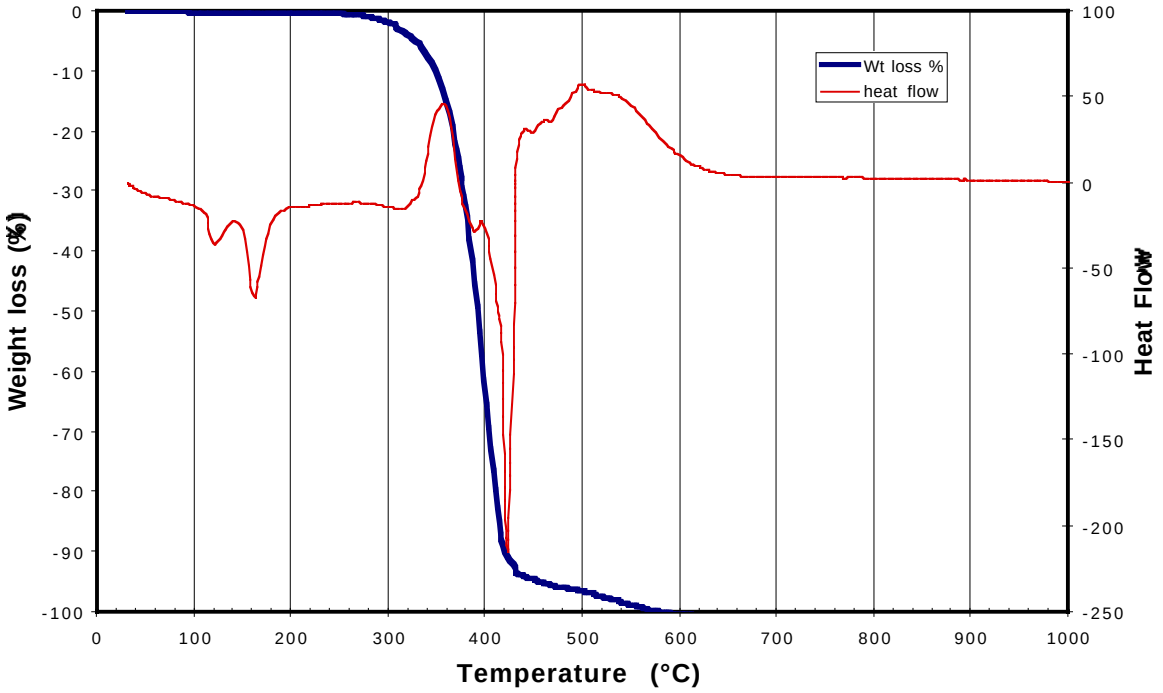


Figure 2 DTA Spectrum for KAOWAX

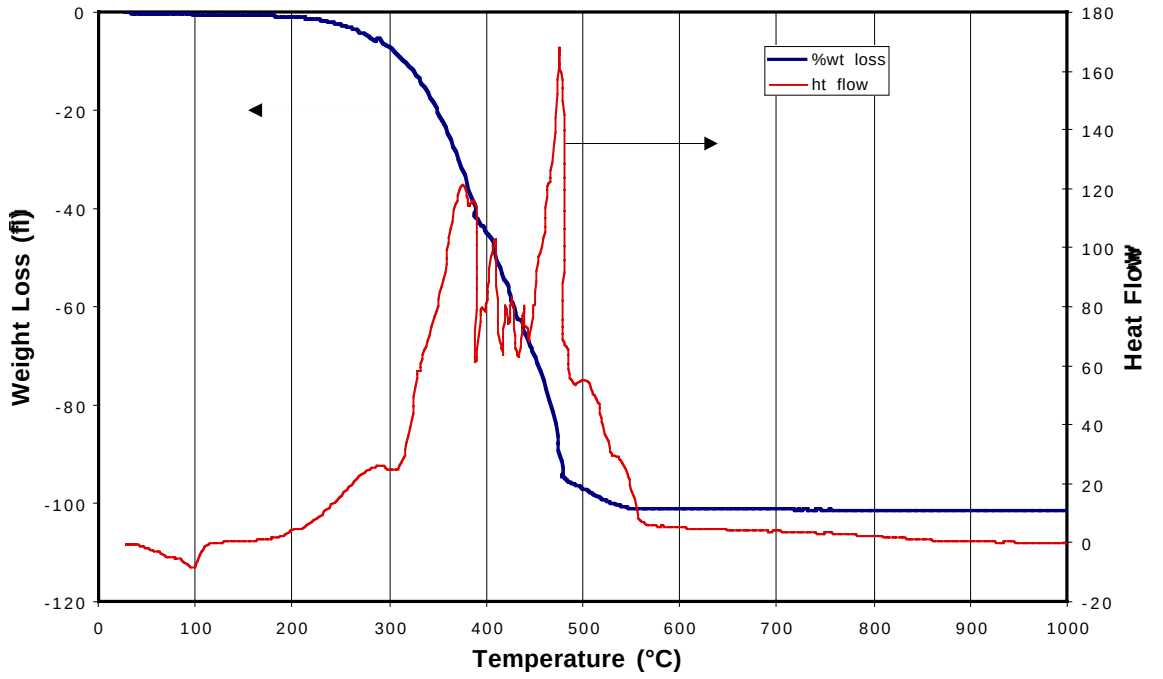


Figure 3 DTA Spectrum for UNIWAX

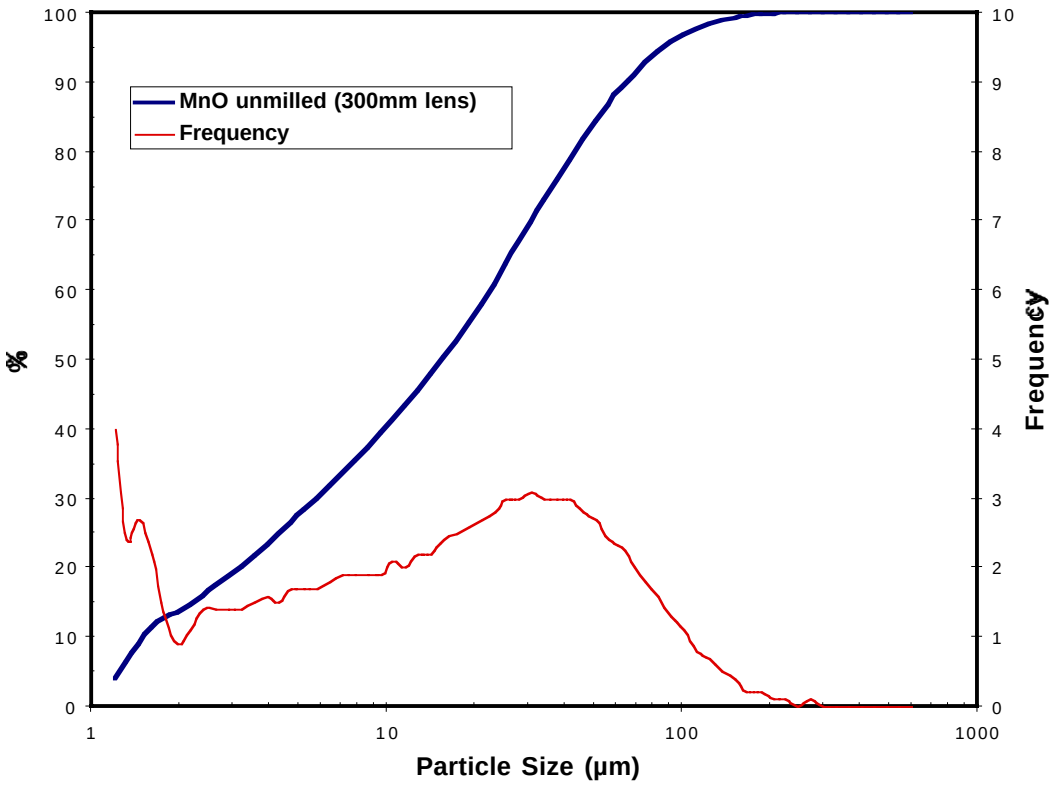


Figure 4 Particle Size Distribution : as-received MnO powder (1 – 1000 µm). Lens size referred to is that used for measurement on the Malvern Mastersizer Instrument used for this particle size analysis.

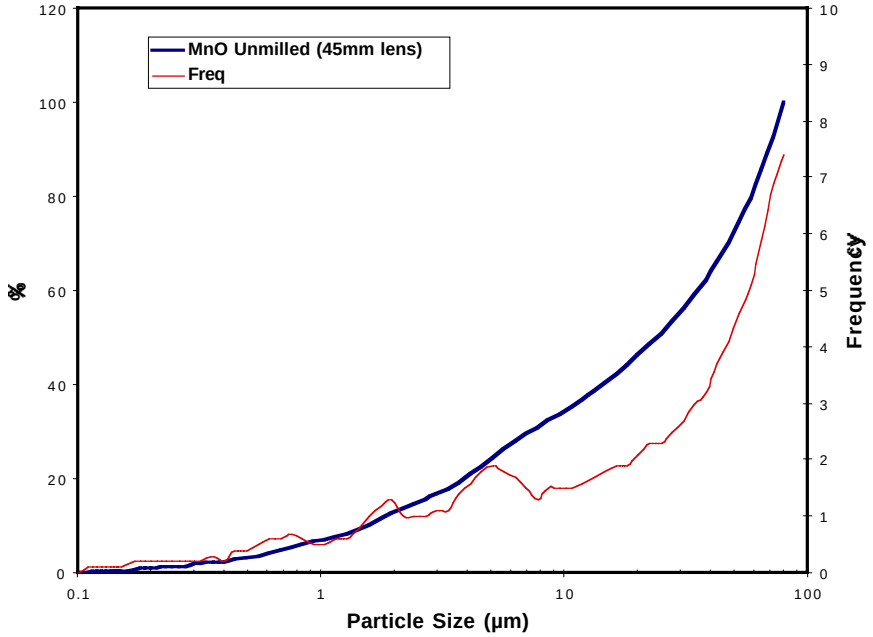


Figure 5 Particle Size Distribution : as-received MnO powder (0.1 – 100 µm). Lens size referred to is that used for measurement on the Malvern Mastersizer Instrument used for this particle size analysis.

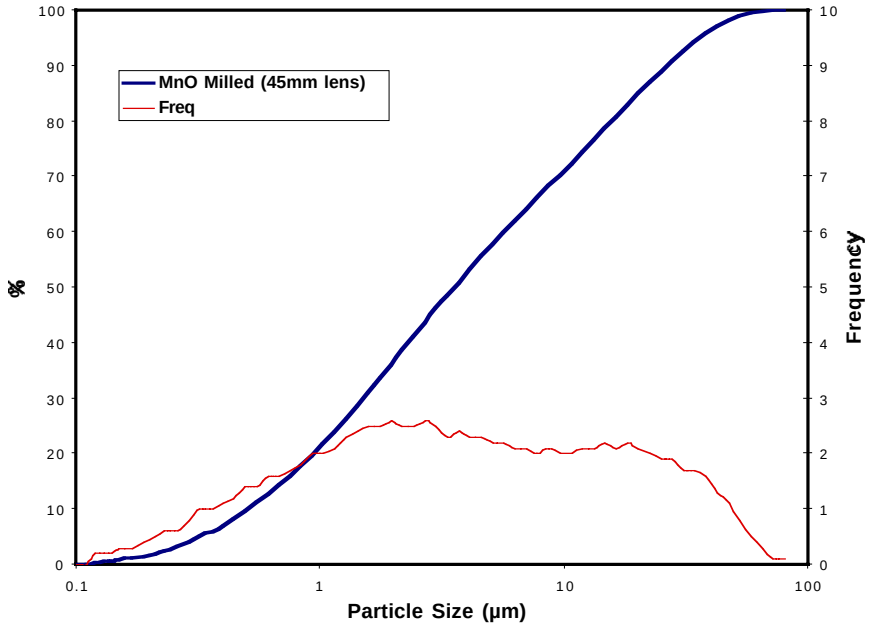


Figure 6 Particle Size Distribution : Attrition-milled MnO powder (0.1 – 100 µm). Lens size referred to is that used for measurement on the Malvern Mastersizer Instrument used for this particle size analysis.

Table 1 Blending Baseline Composition A-0 with 1 % KAOWAX addition

Run (100g / run)	Torque (Nm) after 30sec	Power (HP) after 30sec	Temperature (°C) after 5 mins centre – wall temp.	Recovery (g)
1	18.8 – 19.2	1.10	-	62.00
2	16.6 – 17.7	1.04	66	67.20
3	17.2 – 18.8	1.09	78	100.61
4	17.1 – 18.2	1.08	81	111.53
mill allowed to cool down to 20°C				
5	16.8 – 17.4	1.07	46	118.92
6	16.3 – 17.2	1.06	60	89.05
7	17.2 – 18.2	1.10	73	103.82
8	17.6 – 18.8	1.12	80	89.78
9	17.9 – 18.8	1.12	90	95.97
10	17.9 – 18.9	1.15	100	111.64
11	No additional powder added, mill time 6 mins			41.46
			Total	967.27

Table 2 Granulation Runs prior to 15/04/99

Run #	Powder #	Binder
G112	TEX991009B	5 % Elvanol (Dupont) Powder
G113	TEX991006B	5 % Elvanol (Dupont) Powder
G114	TEX991007B	25 % Daystar PVA Solution

Table 3 Sintering of Pucks prior to 15/04/99

	SLD Run #	A990413	A990416
Mass (g)	Initial	401.00	388.50
	Final	354.10	353.3
	% Difference	11.70	9.06
Diameter (mm)	Initial	90.30	90.3
	Final	66.47	69.19
	% Difference	26.39	23.38
Thickness (mm)	Initial	33.60	26.52
	Final	24.60	20.32
	% Difference	26.79	23.38
Geometrical Density (g/cm^3)	Initial	1.86	2.29
	Final	4.15	4.63
	% Difference	55.07	50.53
	% Theoretical Density	79	89

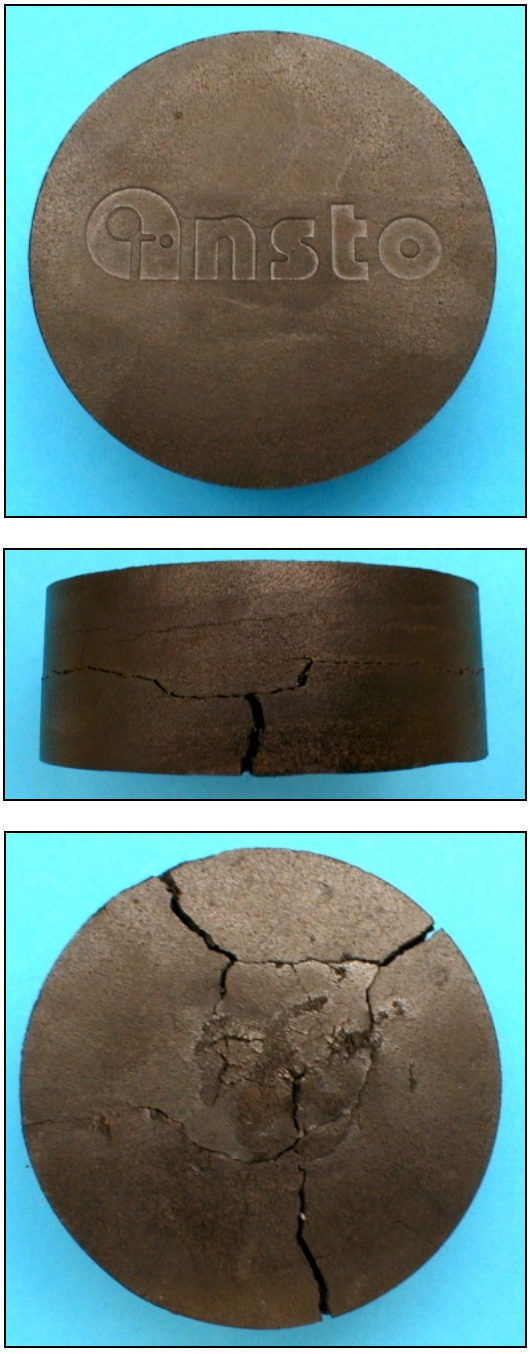


Figure 7 Photographs of Sintered Puck A990413 (Ø67mm)

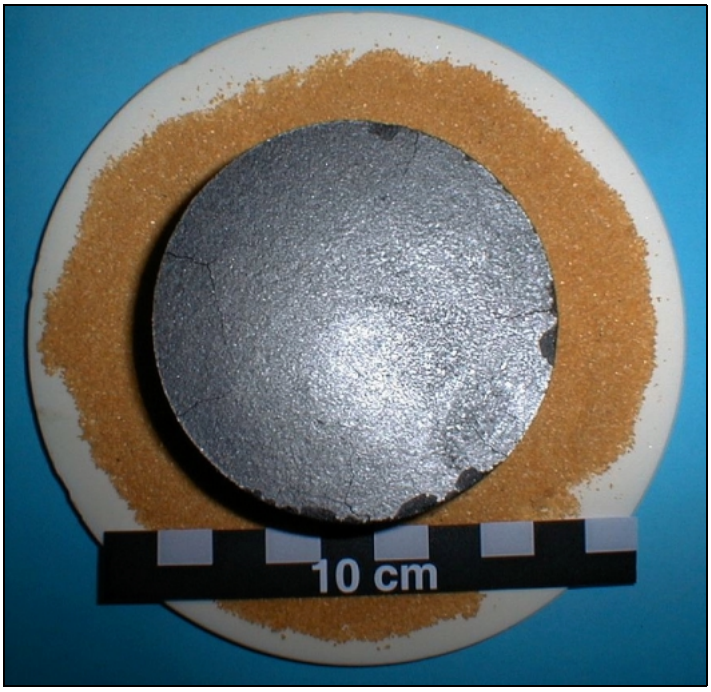
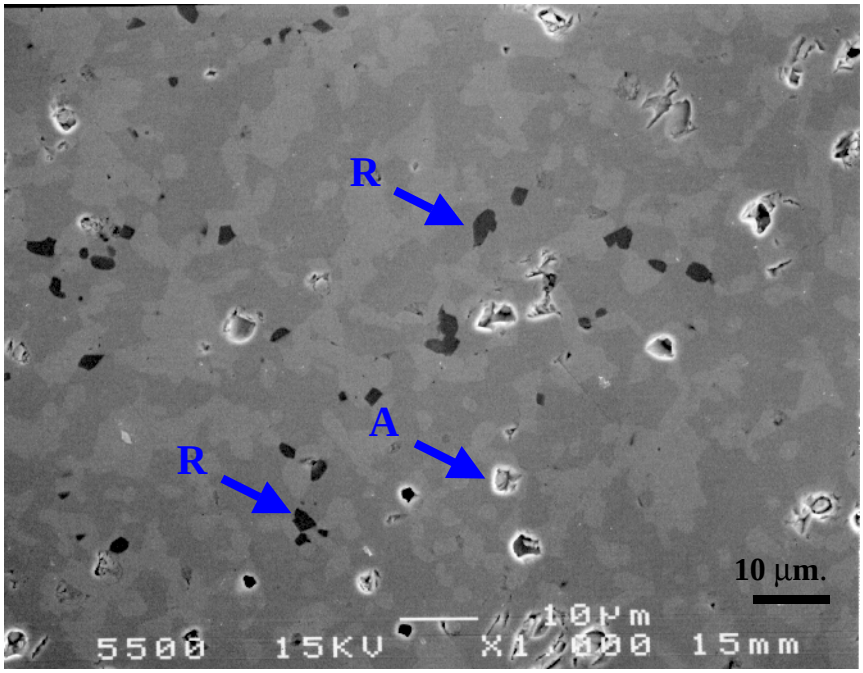


Figure 8 Photograph of Top Surface of Sintered Puck A990416 (Ø69mm)

(a)



(b)

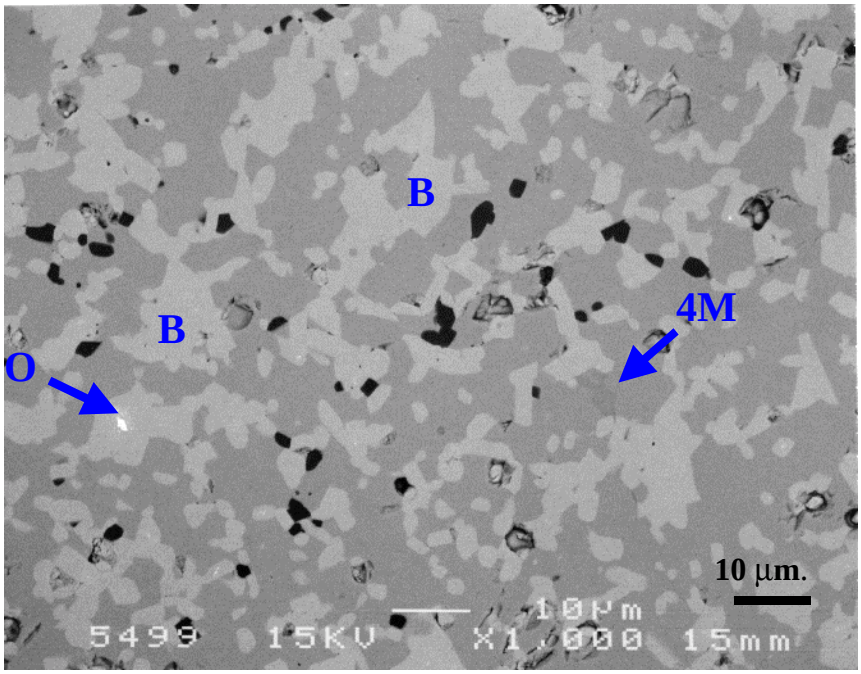
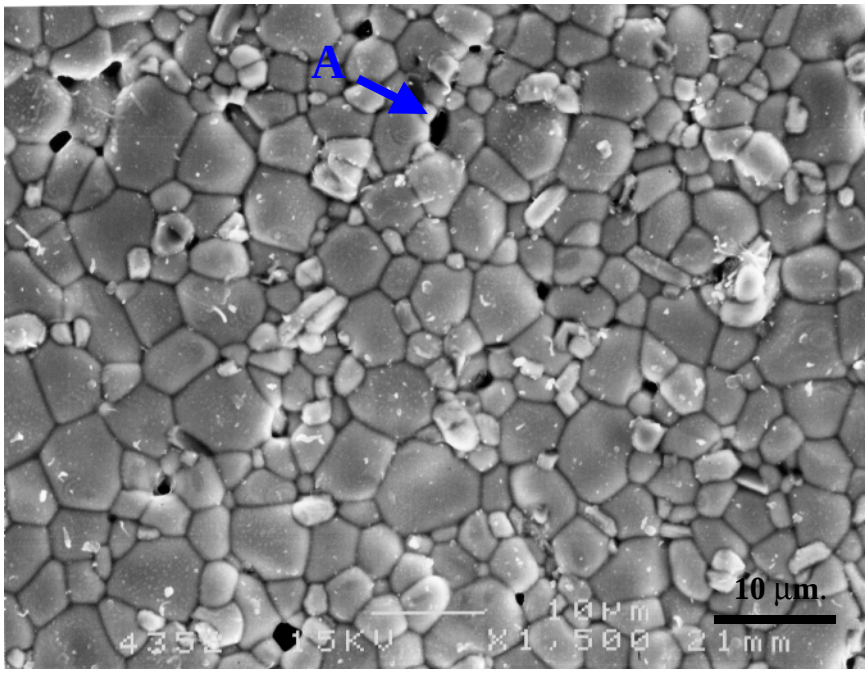


Figure 9

(a) Secondary electron micrograph and (b) backscattered electron micrograph of polished internal section of mws980137, a Ø10 mm pellet (Task 1.2, composition B1-2, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore. Th / U-brannerite (B, light grey grains), Hf-doped rutile (R, dark-grey), a trace of 4M zirconolite (4M), a grain of ThO_2 (O, white) and porosity (A) are also present.

(a)



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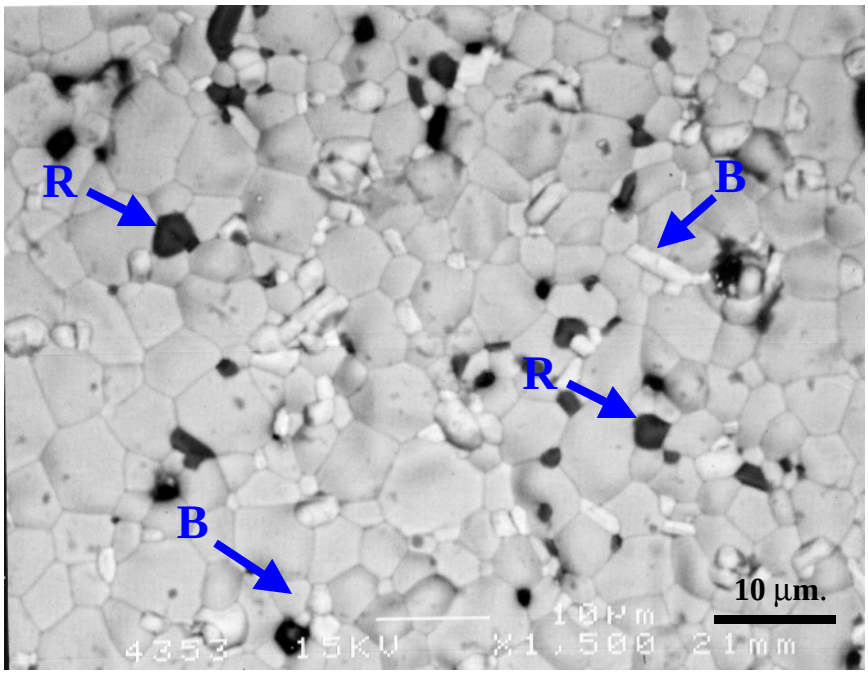

Figure 10

(a) Secondary electron micrograph and (b) backscattered electron micrograph of top surface of mws980434, a Ø25 mm pellet (Task 1.2, composition B1-2, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). Phases detected on the surface were pyrochlore (the grey matrix), Th / U-brannerite (B, light grey grains) and Hf-doped rutile.